

Passive Anoxic Limestone Drains

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A handwritten signature in cursive script, reading "Garry McKenzie", is written over a horizontal dashed line. A long, thin horizontal line extends from the end of the signature to the right edge of the page.

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ABSTRACT

A passive anoxic limestone drain is an effective and relatively inexpensive, long-term method of treating acid mine drainage. A PALD raises the pH of acidified waters and introduces alkalinity, which provides a buffer against further changes in pH caused by the oxidation and hydrolysis of iron. The systems can be designed to work in a variety of geologic and topographic settings. The PALD currently functioning in Perry County, Ohio has been successful in raising the pH of the raw drainage at an abandoned strip mine.

INTRODUCTION

The purpose of this paper is to describe how a passive anoxic limestone drain treats acid mine drainage, and to discuss the system currently in use in Perry County, Ohio.

Kirk Beech and Jim Gable of the Ohio Department of Natural Resources provided test results, blueprints and background information for the Perry County site. Their cooperation is gratefully acknowledged. My thanks are also extended to Garry McKenzie for his advice, comments and support, and to Gunter Faure for reviewing and commenting on the chemical reactions which are described in this paper.

Acid mine drainage (AMD) is a serious problem associated with surface and underground coal mining. The problem is caused by the oxidation of pyrite within the mine spoil, and the subsequent oxidation of ferrous iron and precipitation of ferric iron hydroxides, which causes both a pH level decrease, and an increase in the

dissolved metal content, producing conditions toxic to most life forms. The Tennessee Valley Authority has been treating acid mine drainage with constructed wetland treatment cells and/or settling ponds, where microbiologic ferrous oxidation, hydrolysis and precipitation of iron hydroxides take place in a restricted environment. While the wetland treatment cells remove substantial amounts of iron from the water, pH levels may fall as low as 2.0 s.u. during the process, leading to poor effluent water quality (Narin et al., 1991). The use of chemical additives to lower the pH of AMD is expensive and may harm aquatic life in receiving streams, thus the idea of introducing buffering capacity into the drainage by passive means is an attractive alternative (Turner and McCoy, 1990).

A passive anoxic limestone drain (PALD) is a relatively new technology now in use to treat mine drainage. A PALD system is a sealed trench filled with limestone and capped with impermeable clay which creates a reducing environment for AMD to flow through. The principle behind the system is that if acidic, ferrous-iron-enhanced waters come into contact with limestone in an anoxic environment, the limestone will dissolve, raising the pH and introducing alkalinity into the water, thus buffering it against further pH changes caused by precipitation of the metal hydroxides. Once the water reaches the atmosphere, iron oxidation and precipitation reactions occur at the effluent pipe and within a settling pond. The treated water can then be discharged into the local watershed. Most PALDs have an average one time cost of less than \$10,000. For chemical treatment methods, \$20,000 is needed to

purchase the NaOH and another \$10,000 is expended in annual operating costs. The basic PALD design is given in Fig.1.

The system was discovered by accident, when a TVA worker found that waters reaching a wetland treatment cell had elevated pH levels. Investigations revealed that a clay dam had been constructed over an old coal haul road which was made of high grade crushed limestone. The waters percolating through the limestone, beneath the dam were being treated before reaching the wetland system (Brodie et al., 1990).

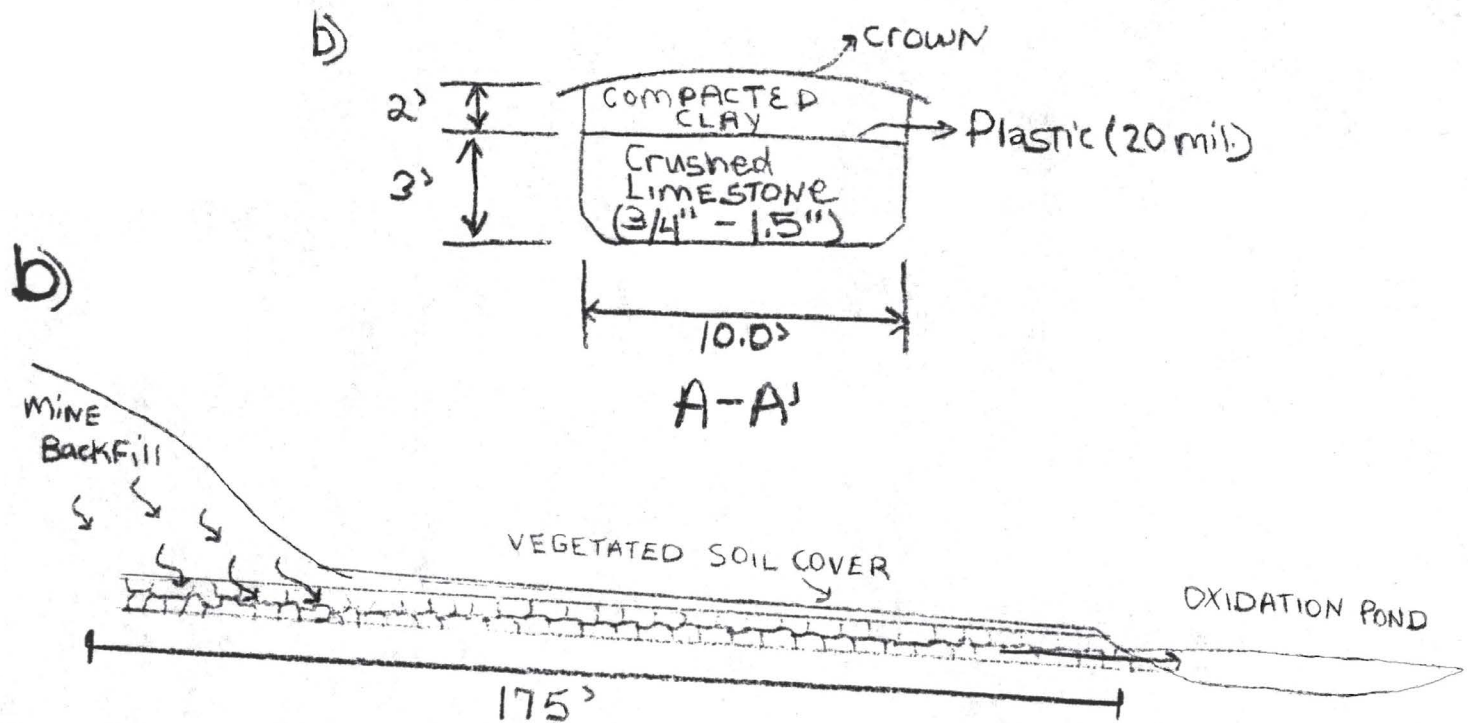


Figure 1: Design of a typical PALD

a) and b) cross section.

Modified from: Brodie et al., 1990

DESIGN CONSIDERATIONS

The width, depth and length of the system are a function of topography, geology, accommodation of maximum expected flow levels and desired longevity of the drain (Narin, undated). Discrete seeps or boils from embankments are ideal for the placement of a system, but underground mines could also be sealed and flooded and the drainage routed through a pipe into a PALD (Brodie et al., 1990). Most existing drains contain a layer of limestone 2-5 ft. deep, are 2-9 ft. wide and 150-1500 ft. long.

Calcite content of the limestone is a particularly important parameter. Brodie suggests that the calcite content of the limestone exceed 90% for best results. Magnesium carbonate dissolves more slowly in weak acids than pure calcite, and may be ineffective in raising pH significantly. Size of the limestone rock is also important. To ensure the maximum surface area and facilitate reaction rates while still maintaining good hydraulic conductivity, the limestone should be of gravel size (0.75-1.5 inch). Finer limestone may cause clogging of the system, while a larger sized rock doesn't react as quickly due to the decrease in surface area.

Reducing conditions must be maintained in the drain to prevent the oxidation and precipitation of oxyhydroxides, namely those of iron, from clogging the drain and rendering it useless. Most drains are lined with 20 mil plastic to prevent oxygen penetration and then covered with a layer of clay or soil at least 2 ft. thick. The clay or soil should be compacted and crowned to accommodate settling and retard

oxygen seepage. The crown is then be planted with grasses to prevent erosion. Trees are undesirable because their roots will penetrate the system and allow oxygen to enter.

At the drain discharge point of a PALD there is usually a settling/oxidation pond where precipitation of hydroxides takes place (see Fig 1, p. 3). Some systems also utilize wetland systems for final iron and manganese removal (Brodie, et al., 1990).

The quantity of mine drainage is an important factor to consider when deciding how best to use PALD to treat an area. Brodie suggested that since the systems are relatively inexpensive to build, overdesign is the best method for insuring that the system's longevity will not be affected by changes in the hydraulic regime. Flow rates of a mine seep can be measured using the bucket and stopwatch method, or by estimating the peak runoff of a basin and the amount of the water that will eventually end up as groundwater and designing the PALD for those rates of flow. As an example, he cited an 11-acre watershed with peak runoff from a 10-year storm event estimated at 20 cfs, with 40% of that runoff entering the ground water regime. Thus the PALD for this watershed should be designed to handle 8 cfs. Although actual groundwater flow in such a watershed will be less than 8 cfs, this method will result in an overdesign of the system, insuring adequate, long-term AMD treatment.

Tests of water chemistry should be conducted before the passive system is introduced. The amount of dissolved oxygen in the mine water can significantly affect drain performance. If DO levels in the waters are above 2-3 mg/L, iron oxidation may take place in the drain, armoring the limestone and halting further reactions. Eh

levels, which are dependent on the availability of oxygen in the system, should be below +300 mV, indicating that the waters are reducing. The pH level should be below 6 s.u. Under higher Eh, pH and DO levels, ferric iron will oxidize and form insoluble ferrous oxyhydroxides within the drain, rendering it ineffective. In this case, alternative treatment methods need to be researched (Brodie et al, 1990).

The acidity load (the amount of acidity a seep will produce per year), and the total mass of limestone needed to neutralize it, can be calculated if the flow rate, the mineral acidity (the total acidic properties of Fe, Al, and Mn in solution), the desired longevity of the drain, the CaCO₃ content of the limestone and the expected amount of dissolution of the limestone are known. The technique is as follows:

$$\text{Acidity load (tons/yr)} = \text{Flow (Lpm)} * \text{Acidity (mg/L)} * 0.5256$$

or, if flow is measured in gallons per minute

$$\text{Acidity load (tons/yr)} = \text{Flow (gpm)} * \text{Acidity (mg/L)} * 0.0022$$

Once the acidity load has been calculated, the desired longevity of the system can be used to calculate the total mass of acidity that the system will need to neutralize over its design life.

$$\text{Acidity mass (tons)} = \text{Acidity load (tons/yr)} * \text{Longevity (years)}$$

To calculate the mass of limestone needed, it is necessary to know the percentage of CaCO₃ in the limestone, the mass of acidity the drain will need to neutralize over its life, and the amount of limestone expected to dissolve.

$$\text{Limestone mass (tons)} = \text{Acidity mass (tons)} / \text{CaCO}_3 \text{ content (\%)}$$

$$\text{Total Limestone mass (tons)} = \text{Limestone mass (tons)} / \text{Expected dissolution}$$

Example: Flow: 10 gpm (moderate flow)

Acidity: 400 mg/L (high acidity drainage)

Acidity load (tons/yr) = $10 \text{ gpm} \times 400 \text{ mg/L} \times .0022 = 8.8 \text{ tons/year}$

(the mine seep will produce 8.8 tons/year of acidity)

if the desired longevity of the system is 50 years :

$8.8 \text{ tons/yr} \times 50 \text{ years} = 440 \text{ tons}$

thus, over a period of 50 years the seep will produce 440 tons of acidity.

If the limestone contains 90% CaCO_3 then:

$440 \text{ tons} / 0.9 = 490 \text{ tons}$ of limestone are required.

This is the amount of limestone needed if total dissolution of the limestone is expected. If only partial dissolution is expected, this number must be divided by the percentage of limestone that is expected to dissolve. If 75% dissolution is expected then:

$490 \text{ tons} / 0.75 = 650 \text{ tons}$

thus, 650 tons of 90% calcite grade limestone is needed to ensure the system will last 50 years (Narin, undated).

The TVA studied dissolution rates of the limestones in its Kingston Fossil Plant in Roane Co., Tenn., and estimated the lifespans of the drains from their data. They filled four 55-gallon barrels with 0.75 in. crushed limestone grading 92% CaCO_3 , and ran acidified mine drainage into the barrels at the bottom and out through the top to insure anaerobic conditions. Flow rates averaged 0.00296 to 0.000862 L/min/kg limestone, but ranged between 0.0 and 0.00321 L/min/kg limestone. They found that increased flow rates decreased the rate of limestone dissolution and the amount of alkalinity in the

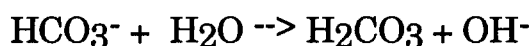
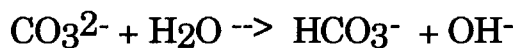
effluent. The limestone dissolution rates were used to calculate the life of each system. Data are listed in table 1 (Brodie et al., 1990).

TABLE 1
Results of the TVA experiment conducted to measure limestone dissolution rates and calculate drain lifespans. Flow rates varied between 0.0 - 0.00321 L/min/kg limestone (adapted from Brodie et al.,1990).

	Inflow	Bbl 1	Bbl 2	Bbl4
pH	5.87	6.75	6.47	6.33
Alkalinity (mg/L)	62.79	143.09	97.02	95.31
Average Flow (L/min/kg limestone)		2.01E-04	4.86E-04	2.96E-03
Test duration (days)		90	90	90
Measured Dissolution rate (g/kg/day)		0.0589	0.0329	0.0644
Expected Longevity <u>(years)</u>		46	83	42

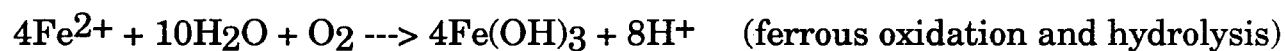
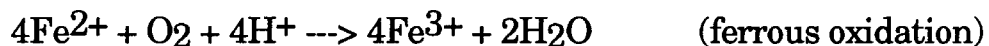
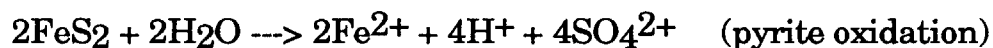
IMPORTANT REACTIONS

When the acidic waters come into contact with the limestone in the trench, the CaCO₃ disassociates:



At pH levels below 6.3, H_2CO_3 is the dominant ion. The introduction of the hydroxide ion into the water raises the pH and provides a buffer against further pH changes, since there is a continuous supply of hydroxide ions from the system.

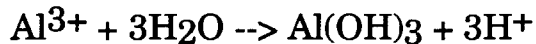
The alkalinity, is vital because it neutralizes mineral acidity. The hydrolysis of the metal cations present in the water, produces H^+ as a byproduct. Brodie et al., (1990) described one wetland treatment system in which the removal of iron from the water caused the pH levels to drop from 6.0 s.u. to less than 3. The most important acidity producing reactions involve iron, manganese, and possibly aluminum. The iron reactions are as follows.



Thus greater concentrations of iron in the drainage water produce more acidity, unless buffered in an anaerobic environment (Brodie, et al., 1990). The reactions occur more quickly at higher pH; if the pH falls below 6, the reactions shift left and the removal of iron is slowed. The insoluble ferric hydroxide is the substance that is precipitated at the effluent of the system. Like iron, manganese removal also occurs more quickly at higher pH. If pH falls below 6 the removal of manganese may cease altogether (Narin et al., 1991).

Precipitation of aluminum is another concern in a PALD system. The precipitation of insoluble aluminum hydroxides involves only hydrolysis and not oxidation, and thus is a function of pH. As the pH of the drainage raises to values between 4.5 and 8.0

s.u., aluminum becomes more stable as insoluble gibbsite, which may precipitate when strongly acidic solutions are neutralized:



Below a pH of 4.5, most aluminum is soluble (Faure, 1991). Some PALD effluents studied have experienced an initial decrease, followed by a small increase in aluminum content, which Narin attributes to formation of particulate aluminum. Whether the hydroxides are forming within the drain or only at the effluent is unknown.

The formation of gypsum is also a theoretical concern. At the concentrations of sulfate and calcium found in many drains, conditions close to saturation may exist and gypsum precipitate may form. Whether gypsum could affect drain function is unknown (Narin et al. 1991).

THE HOWARD WILLIAMS LAKE PROJECT

The Howard Williams Lake PALD is located 3 miles southeast of New Lexington in Perry County (see Fig. 2). The area is locally known as the Sunnyhill Mine.

The region lies on the east side of the Cincinnati arch; bedrock strata dip gently to the east-southeast at 25-30 ft./mile. Prior to 1972, both underground and surface mining took place at the site. The ore mined was the Middle Kittanning coal bed #6 of the Allegheny series in the Pennsylvanian system; it is nearly 42" thick in this area. The area is unglaciated and topography is mature with relief averaging about 200 ft. (Flint, 1951). The soils in the area are channery loams and shaley clay loams (Soil Survey of Perry County, 1984). Because

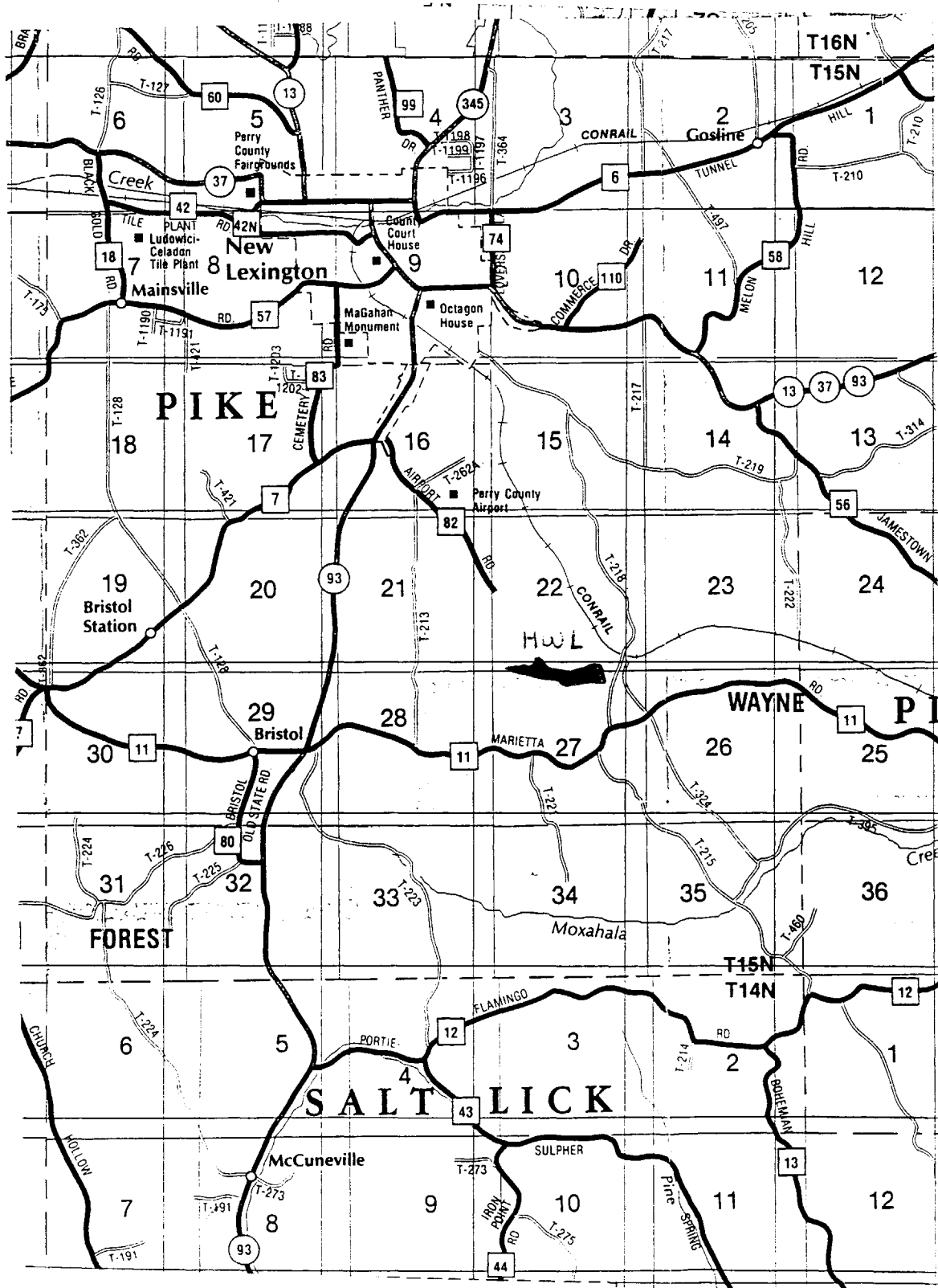
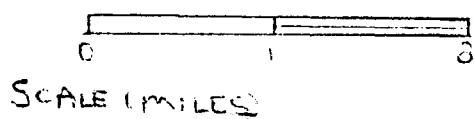


Figure 2: Location of the Howard Williams Lake site, in Perry County, OH.

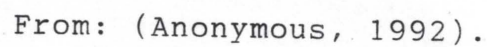


of the poor soils and steep topography, mining has been the major occupation, and now that the mining has ceased, the region is economically depressed.

Originally the area around where the lake now is drained north into the Rush Creek system (Flint, 1951), but mining activities have disturbed the drainage pattern and the area now lies in the headwaters of the Moxahala Creek watershed to the south. The discharge from the lake was considered the largest point source of acid mine drainage polluting the Moxahala Creek watershed.

Reclamation efforts to stop physical pollution of the watershed began in 1990, when a highwall on the north side of the site was backfilled. Spoil reclamation was completed in late 1991 (Anonymous, 1992). Backfilling the highwall and revegetating the spoil did not treat the chemical pollution caused by acidified waters draining from the spoil, and in the fall of 1991 Ohio Department of Natural Resources decided to install a PALD on the north side of the lake. The system was the first one built in Ohio; a second one is now being constructed near the Morgan-Perry County line, at a site known as Tropic. The Tropic site will utilize a wetland system in conjunction with the PALD (Gable, pers. comm., 1993).

The layout of the PALD at HWL is shown in figure 3. A 175-ft-long trench was dug to intercept the water flowing above the level of a coal seam (see Figure 4). The trench is 5 ft. deep and 15 ft. across. The top, bottom and downhill side of the trench were lined with 'mirofi' and another liner of 20 mil plastic was placed on the bottom and downhill side of the trench (see Fig. 3). The trench was then filled with limestone grading 84.3% CaCO_3



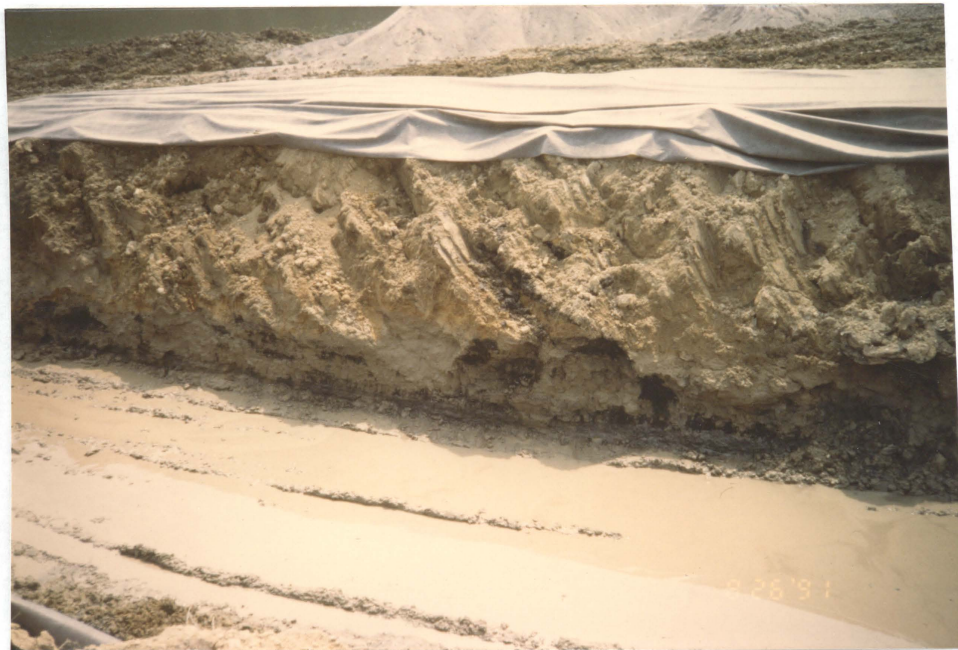


Figure 4. The HWL PALD was built to intercept water flowing above the level of a coal seam.



Figure 5. After construction was completed, the water would not flow through the trench. The trench had to be dug up and resealed



Figure 6: The seep at HWL caused by PALD interrupting the subsurface drainage.



Figure 7: Iron precipitate at the effluent pipe.

(Anonymous, 1991). At 20-ft intervals, perforated, air tight pipes were sunk into the trench, to enable ODNR to monitor water levels in the trench (Gable, pers. comm., 1993).

At the face of the trench, a 5 ft. thick clay dam was constructed to further retard oxygen penetration into the system. The water is channeled through the dam in an 8" PVC pipe, where it flows vertically up through a 6" PVC overflow pipe.

The hydrology of the area was not well studied prior to designing the system. Problems developed in maintaining the water flow through the system after construction (see Fig. 5), and the PALD had to be dug up and resealed (Beech, pers. comm. 1993). Several months later, a seep developed downhill from the system, (see Fig. 6) which has spread to a length of nearly 90 ft. The pH of the seep is less than 3.0, iron hydroxides are forming a ferricrete over the soil, and it's affect on vegetation is obvious from the photo. Because pH levels are low and the seep occurred after installation of the PALD, it is most likely that the PALD interrupted subsurface water flow and as a result, water is circumventing the system somewhere near the head of the trench.

Pre-drain chemical tests were conducted by Ohio Department of Natural Resources and the Peabody Mining Co. The location of the seep that Peabody labs tested is unknown, but its likely that it was near the lake, since reclamation efforts were focused there. Test results are shown in Table 2, p. 14. Dissolved oxygen content of the seep was not measured. Note the low, dissolved iron and manganese in the lake discharge. The differences in metal concentrations and

pH between the samples indicate that in the lake, hydrolysis and precipitation of metals in an unbuffered solution were taking place.

In March of 1992 the first tests of the water exiting the PALD system were made. The samples were taken at the effluent pipe, and tested by Coshocton Environmental Testing, Inc. All samples were collected by Jim Gable of the Zanesville ODNR. Results of selected dates are summarized in Table 3, p. 15. Care must be taken in comparing the data for the lake discharge against the data on the samples taken from the PALD effluent pipe. Precipitation of metal hydroxides occurs within the lake, but not within the PALD system, thus water environments differ. The only valid that can be made is a comparison is between the seep water and the PALD effluent, since neither had reacted with the lake waters. No tests have been done on water quality of the lake discharge since the PALD became fully functional.

The iron precipitates at the effluent pipe and within the lake (see Fig. 7). It forms a 'ferricrete' over soil, and coats the pipe where the water velocity is lowest. The system is not aesthetically pleasing. Eventually the lake will have to be dredged and the oxyhydroxides and other precipitates will have to be disposed of, however that problem has not yet been addressed.

Effects of the system in treating pH levels were immediate and obvious. Except for the April results, the system has maintained pH at levels near 6.0 s.u., and provided a reducing environment to keep iron from oxidizing to the ferric state within the drain.

Table 2
Water quality at Howard Williams Lake, (1)
during recalamation, and (2) when the PALD
was installed.

	SEEP ¹	LAKE DISCHARGE ²
pH (s.u.)	3.86	2.82
Acidity (mg/L)	1745.2	-nt-
Specific Conductivity (umho/cm)	5449.0	2970.0
Iron, total (mg/L) ^{0 3}	570.0	76.2
Manganese, total (mg/L)	98.0	37.0
Aluminum, total (mg/L)	-nt-	22.6
Sulfate (mg/L)	4736.0	1640.0

1. Water tested by Peabody Labs, Sept-Oct 1991,
exact location of the seep unknown.

2. Water tested by ODNR, Mar. 1992, locality listed as lake
discharge, east end of HWL.

-nt- not tested

TABLE 3

Water quality test results for selected dates, samples taken from the PALD effluent pipe, located on the north shore of Howard Williams Lake. Compare with the seep data in Table 2.

Date	3-27-92	4-27-92	6-12-92	8-10-92
pH (s.u.)	5.58	3.97	5.68	5.78
Acidity (mg/L)	1052.0	1135.0	1050.0	969.0
Iron, total (mg/L)	744.0	828.0	612.0	680.0
Manganese, total (mg/L)	98.0	98.6	96.6	92.8
Aluminum, total (mg/L)	1.89	0.7	2.2	1.53
Sulfate (mg/L)	4420.0	4070.0	4285.0	4 321.0
Iron (Fe ³⁺) (mg/L)	8.0	120.0	37.0	28.0

The April test results indicate that oxygen somehow entered the system. The ratio between Fe²⁺ and Fe³⁺ increased, thus ferrous iron was being oxidized to the ferric state, which in turn lowered the pH. The specific conductivity rose, indicating the presence of higher amounts of dissolved metals in the water. Water oxygen levels could have been raised by a leak in the system or by an increased amount of dissolved oxygen in the water. The latter is most likely since testing done after April showed pH back to levels near 6.0 s.u.

Despite the improvement in iron emissions, the mine water is still not to EPA standards for iron emission, which is 1 mg/L. According to one EPA worker, iron is such a problem at old coal mine sites, that water quality standards for iron are never achieved (Heitzman, pers. comm., 1993).

Aluminum content at the effluent is very low. Aluminum precipitate may be forming inside the system, but whether this will armor the limestone and affect the life of the drain remains to be seen. The Federal EPA sets toxicity standards for aluminum at 0.750 mg/L (Heitzman, pers. comm., 1993).

Manganese doesn't seem to be affected by passage through the drain, although some appears to be precipitating within the lake. At this time the EPA has no set standards for manganese emissions from mine sites, and it is unknown how elevated manganese levels affect aquatic life.

CONCLUSIONS

The PALD at the Howard Williams lake site has been successful in improving the quality of the mine drainage. Because of the extremely polluted nature of the raw drainage, the water will probably never be excellent, but the increase in pH levels may help reestablish some aquatic life downstream.

The system needs further study both to determine its impact on areas downstream from the lake. The lake discharge also needs further study to determine how successful the buffered waters are in preventing pH decrease after iron precipitates, and to measure the

lake water's dissolved metal content. During my visits to the site, I noted no aquatic life in the lake.

Since no calculations on acidity load or drain longevity were done prior to installation of the PALD, its life span is unknown. According to Gable (pers. comm., 1993) the system was not expected to last more than a “few” years. Currently, it has been treating the mine seepage for two years.

Aluminum reactions associated with the system also need further study. It is unknown if aluminum precipitates within PALD systems. Pieces of the limestone can be retrieved through the PVC pipes at HWL, and their coatings (if any) analyzed for aluminum content to determine what effect the aluminum ion has on the longevity of a limestone drain.

Preliminary results of the system look promising for treating AMD on a small scale. The system is an environmentally sound and relatively inexpensive way of solving water quality problems associated with acid mine drainage.

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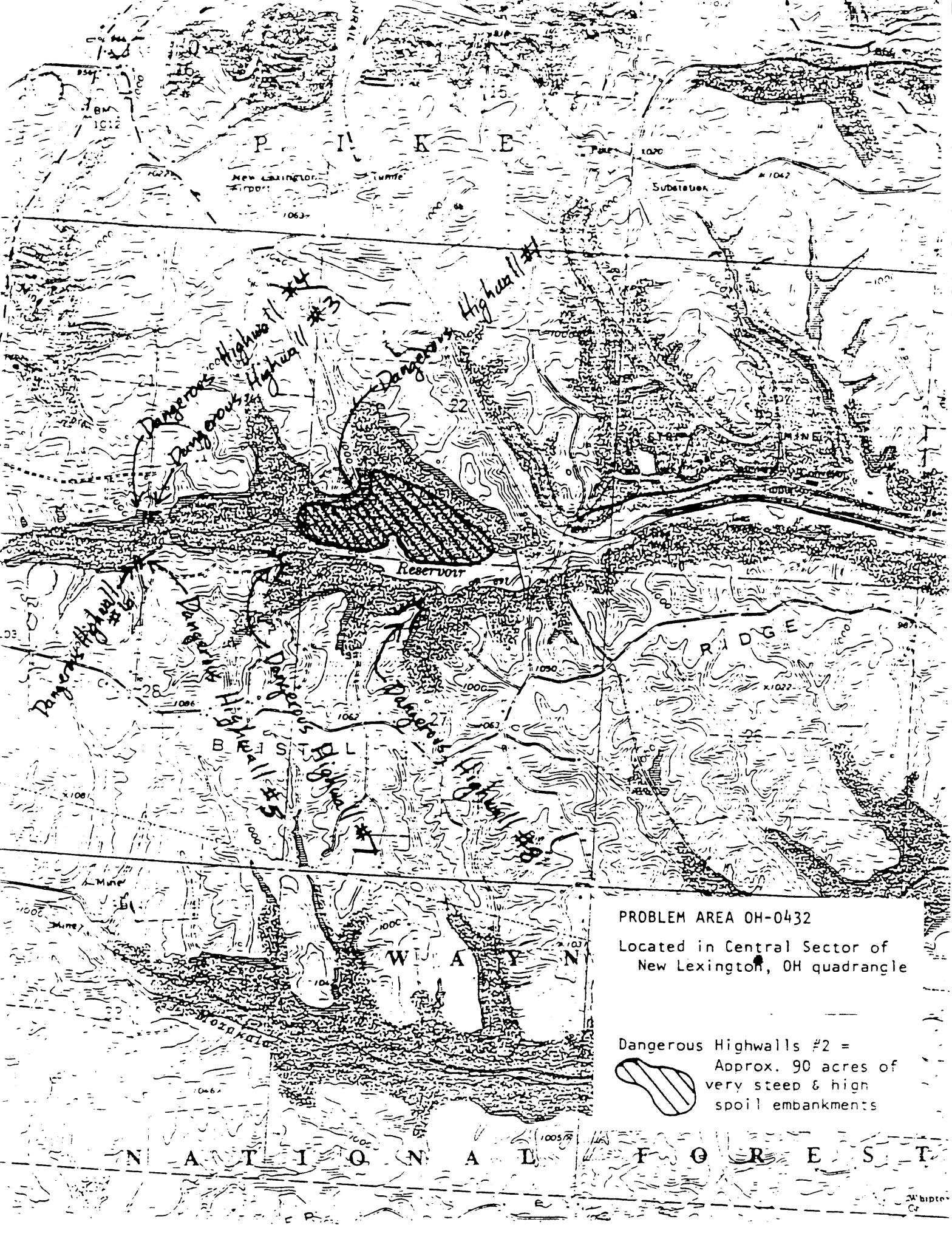
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Test results, AML Howard Williams Lake, 3-27-92 through 8-10-92.

Samples collected by Jim Gable, ODNR, Zanesville. Samples tested by Coshocton Environmental Testing, Inc.

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P I K E

New Lexington
Airport

Substation

Reservoir

RIDGE

W A T Y N

PROBLEM AREA OH-0432

Located in Central Sector of
New Lexington, OH quadrangle

Dangerous Highwalls #2 =
Approx. 90 acres of
very steep & high
spoil embankments



N A T I O N A L F O R E S T

	2,315
FEDERAL PROJECT	163,800
	421,315

